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Molecular Structure of Interphases Between DGEBA/BTDA
Adhesives and Silver Substrates Using Surface-Enhanced
Raman Scattering

by

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flat configuration. SERS spectra obtained from a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured against a silver substrate using BTDA as the curing agent were identical to SERS spectra of BTDA and were independent of the epoxy/BTDA ratio, indicating that the spectra were characteristic of the interface rather than the bulk adhesive and that BTDA was preferentially adsorbed onto the silver substrate. SERS spectra obtained from thin films of BTDA adsorbed onto silver and then overcoated with thick films of epoxy were identical to spectra of BTDA and showed no evidence of bands related to DGEBA, supporting the conclusion that the SERS spectra obtained from the DGEBA/BTDA adhesive were characteristic of the interfacial region.

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Abstract

Surface-enhanced Raman scattering (SERS) was used for the non-destructive characterization of interphases between epoxy/anhydride adhesive systems and silver substrates. Normal Raman spectra of benzophenone tetracarboxylic dianhydride (BTDA) were characterized by strong bands near 1785 and 1860 cm^{-1} that were assigned to the anhydride groups, a strong band near 1690 cm^{-1} that was assigned to the benzophenone C=O stretching mode, and by a strong band near 1620 cm^{-1} that was attributed to vibration $\nu(8b)$ of the benzene rings. The bands due to $\nu(8b)$ and to the benzophenone C=O stretching mode were prominent in the SERS spectra of BTDA but the bands related to the anhydride group were missing, indicating that the anhydride groups were hydrolyzed at the silver surface to form carboxylate groups. A band related to a CH out-of-plane bending mode which was absent from normal Raman spectra of BTDA was strong in the SERS spectra, indicating that the molecules were adsorbed onto silver with a flat configuration. SERS spectra obtained from a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured against a silver substrate using BTDA as the curing agent were identical to SERS spectra of BTDA and were independent of the epoxy/BTDA ratio, indicating that the spectra were characteristic of the interface rather than the bulk adhesive and that BTDA was preferentially adsorbed onto the silver substrate. SERS spectra obtained from thin films of BTDA adsorbed onto silver and then overcoated with thick films of epoxy were identical to spectra of BTDA and showed no evidence of bands related to DGEBA, supporting the conclusion

that the SERS spectra obtained from the DGEBA/BTDA adhesive were characteristic of the interfacial region.

KEYWORDS: Raman scattering, surface-enhanced; adhesives, epoxy/anhydride; benzophenone tetracarboxylic dianhydride; diglycidyl ether of bisphenol-A; interphases; durability.

I. Introduction

The term "interphase" is frequently used to describe the transition zone between the surface of a substrate and the bulk of a polymer that is cured or solidified against the substrate (1). In this zone, the chemical and physical properties of the polymer may be considerably different than in the bulk of the polymer. The interphase is responsible for transferring the stress from one adherend to another in adhesive joints and is frequently the site of environmental attack. As a result, it is essential to develop techniques for controlling and characterizing the molecular structure of interphases in adhesive joints. However, few investigations concerned with the molecular structure of interphases in adhesive joints have been reported.

Carter et al (2) investigated the surface chemical effects between electrogalvanized steel (EGS) and low carbon steel (LCS) adherends bonded with an epoxy/dicyandiamide adhesive. They found that lap joints made with EGS adherends were more durable than joints made with LCS adherends during cyclic corrosion testing. Reflection-absorption infrared spectra obtained from steel, zinc, and zinc oxide substrates coated with the epoxy/dicyandiamide adhesive deposited from dilute solutions in dimethylformamide showed that the substrates exerted a strong influence on the molecular structure of the interphase. Carter suggested that a redox reaction between metallic zinc and dicyandiamide resulted in formation of a unique molecular species in the interphase. However, no reaction was noted between zinc oxide and dicyandiamide. It was concluded that zinc was oxidized

and dicyandiamide was reduced when dicyandiamide was cured against metallic zinc.

Kim (3) investigated adhesive joints prepared by curing polyimide films on copper substrates at 400°C and showed that copper-rich particles were distributed in the polymer matrix 80 to 200 μm away from the interface. It was suggested that the polyamic acid precursor reacted with the oxidized copper surface during the cure cycle, producing the particles. When copper was deposited on polyimide, the results were considerably different and a sharp interface was obtained. The peel strengths of joints prepared by curing polyimide against copper and those of joints prepared by depositing copper on cured polyimide were considerably different and correlated with the interphase morphologies.

Garton (4,5) used attenuated total reflection infrared spectroscopy (ATR) to characterize the molecular structure of an anhydride/epoxy adhesive cured at 150°C for 3 hours against an oxidized germanium crystal primed with an amimosilane coupling agent. Garton found that the amino groups of the primer reacted with the anhydride groups in the curing agent to produce amide groups in the interphase. However, there was no evidence of imide formation. Garton concluded that the water produced in the imidization reaction would not be able to escape, thus resulting in an unfavorable equilibrium for imide production.

Crompton (6) used transmission electron microscopy (TEM) to determine the morphological features of the interphase formed when an epoxy adhesive was cured against aluminum. A transition

region between the interface and the bulk of the adhesive was observed in which the physical and chemical properties of the adhesive differed from those of the bulk. Two types of transition layers were observed. The first extended up to a micron from the interface. The other extended only about 100 Å. Pretreatment of the substrate prior to bonding appeared to have little effect of the formation of the transition layers. However, Crompton did not determine the molecular structure of the interphases he observed.

Boerio and Ondrus (7) determined the molecular structure of interphases formed when model epoxy/anhydride and epoxy/tertiary amine adhesives were cured against metal substrates that were pretreated with thin primer films of γ -aminopropyltriethoxysilane (γ -APS). When the tertiary amine curing agent was used, little interdiffusion between the silane and the adhesive occurred and a relatively sharp interface was obtained. However, evidence for oxidation of the aminosilane in the interphase to form an imine was observed.

When the anhydride curing agent was used, there was considerable interdiffusion with the silane and an interphase with a complex molecular structure was obtained. The anhydride reacted with the silane to form amide and imide structures. Some evidence for formation of metal salts by reaction of the anhydride with the oxidized surface of the metal substrates was also observed (7).

Boerio and Ondrus also determined the molecular structure of interphases formed when epoxy/anhydride adhesives were cured

against unprimed copper and copper-containing aluminum substrates (8). Adhesive joints were prepared by curing beams of epoxy against polished substrates at elevated temperatures. When the joints were immersed in liquid nitrogen, the residual stresses were sufficient to enable cracks to be propagated very near the interface, exposing the substrate and adhesive failure surfaces for analysis. Results obtained from x-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) showed that the anhydride curing agent reacted with the cuprous oxide on the copper substrates. Cuprous ions were removed from the oxide and oxidized, resulting in the formation of a layer of cupric carboxylate salt in the interphase. The anhydride adsorbed onto the surface oxide of the 2024 aluminum substrates, which was mostly Al_2O_3 , to form a surface carboxylate. However, no metal ions were removed from the oxide and no layer of metal carboxylate was formed. Copper in the 2024 aluminum was mostly in the form of an aluminide below the surface oxide and did not react with the anhydride.

Boerio et al (9) used a novel technique known as surface-enhanced Raman scattering (SERS) to characterize the interface between a model anaerobic acrylic adhesive and silver substrates. SERS is a process in which the Raman scattering cross section of molecules adsorbed onto the surfaces of metals such as silver, copper, and gold is increased by as much as six orders of magnitude compared to the cross section for normal Raman scattering from the bulk. However, the enhancement is short-range and is restricted to the first few layers of molecules

adjacent to the surface. As a result, SERS can be used to characterize adsorption of organic compounds onto metals and can be used for non-destructive characterization of interphases between polymer films and metal substrates as long as the polymer films are not so thick that normal Raman scattering from the bulk of the film is more intense than SERS from the interphase.

The model anaerobic acrylic adhesive consisted of the monomer triethylene glycol dimethacrylate (TRIEGMA) and a redox cure system composed of acetylphenylhydrazine (APH), o-benzoic sulfimide (saccharin or BS), and cumene hydroperoxide (CHP) (9). This adhesive is known to cure rapidly in the absence of oxygen and in the presence of certain metals such as copper and iron. However, cure in the presence of other metals such as aluminum and zinc is much slower.

SERS spectra were obtained from thin films spin-coated onto silver island films from the neat adhesive and from 1% and 5% solutions of the adhesive in acetone. The spectra all had approximately the same intensity even though the films from which they were obtained had much different thicknesses, indicating that the observed SERS signal was characteristic of the interface and not of the bulk films. Moreover, the SERS spectra observed for the acrylic adhesive had little resemblance to normal Raman spectra of the monomer. Instead, they were similar to SERS spectra of saccharin and to normal Raman spectra of saccharin salts, indicating that saccharin in the adhesive segregated to the interface and adsorbed by dissociation to form a salt.

When saccharin was replaced in the adhesive with benzoic acid and the adhesive was spun onto a silver island film from a 1% solution in acetone, the SERS spectra obtained were virtually identical to SERS spectra of benzoic acid and normal Raman spectra of benzoate salts, indicating again that acidic compounds from the adhesive preferentially adsorbed onto the metal substrate by dissociation to form metal salts.

The salts formed by the adsorption of acidic components of the cure system such as saccharin and benzoic acid onto the metal substrates are thought to play an important role in the cure process (10). During curing, metal ions in the salts are oxidized and the peroxide (CHP) is reduced, providing a source of radicals to initiate polymerization.

Boerio and Hong also used SERS to characterize interphases between an epoxy/dicyandiamide adhesive and silver substrates (11). Spectra obtained from thin films of dicy adsorbed from dilute solutions onto silver island films were characterized by very strong bands assigned to in-plane vibrations and very weak vibrations related to out-of-plane vibrations, indicating that dicy was adsorbed with a vertical configuration involving coordination through the nitrilo nitrogen atom. SERS spectra were obtained from model adhesives consisting of 8:1 mixtures of diglycidyl ether of bisphenol-A (DGEBA) and dicy spin-coated from solutions in dimethylformamide onto silver island films. The spectra were identical to SERS spectra of dicy, indicating that dicy was preferentially adsorbed from the adhesive onto the silver surface and that the interphase in epoxy/dicy adhesives

was likely to have composition that was enriched in dicy when compared to the bulk adhesive.

Some evidence for adsorption of both DGEBA and dicy was observed in SERS spectra obtained from 500:1 mixtures of DGEBA and dicy spin-coated onto silver island films from dilute solutions in DMF, indicating that in those cases there was insufficient dicyandiamide available to occupy all the SERS-active surface sites.

Results described above indicate that interphases can have much different molecular structures than bulk adhesives and that SERS is a powerful technique for determining the molecular structure of interphases. The purpose of this paper is to report results obtained using SERS to determine the molecular structure of interphases between an epoxy cured with benzophenone tetracarboxylic dianhydride (BTDA) and silver substrates. The results indicate that BTDA is preferentially adsorbed onto the substrate to form carboxylate salts.

II. Experimental

Samples were prepared for SERS investigations as described below. Glass slides were immersed in 0.1N NaOH and in 0.1N HCl aqueous solutions for one hour. The slides were then rinsed in distilled-deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol several times, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Silver wire was wrapped around a

tungsten filament which was slowly heated resistively to evaporate island films onto the glass substrates at a rate of about 1 Å/sec. A quartz crystal oscillator thickness monitor was used to control the thickness of the island films at about 40 Å.

Thin films of benzophenone tetracarboxylic dianhydride (BTDA) (Aldrich) were deposited on the silver island films by spin-coating from solutions in dimethylformamide.

SERS spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The slit settings of the monochromator provided a spectral resolution of 10 cm^{-1} for the SERS spectra. The green line of the laser (5145 angstroms in wavelength) was incident on the sample at an angle of about 65° relative to the normal of the sample surface for SERS experiments and was s-polarized. Scattered light was collected using an f/0.95 collection lens and focused onto the entrance slits of the monochromator. Spectra were obtained using a scan speed of 50 cm^{-1} per minute and time constant of either 2 or 10 seconds. Plasma lines were removed from the spectra by the placement of a narrow-bandpass filter between the laser and sample.

Normal Raman spectra were obtained from a small amount of powdered sample supported in a glass capillary tube using the instrument described above and techniques which have been described elsewhere (12). All of the instrumental parameters were the same as used for the SERS spectra except that the slits were set for a spectral width of 5 cm^{-1} .

Samples were prepared for infrared spectroscopy by mixing a small amount of BTDA with KBr and pressing the powder into a pellet under pressure. Infrared spectra were obtained using a Perkin-Elmer 1800 Fourier-transform spectrophotometer.

III. Results and Discussion

The normal Raman spectrum of benzophenone tetracarboxylic dianhydride (BTDA) is shown in Figure 1. Bands observed in the normal Raman spectra are summarized in Table I along with bands observed in the infrared spectra and proposed assignments. Most of the prominent bands in the spectra were assigned using Hase's results for phthalic anhydride as a guide (13).

Bands near 1860 and 1785 cm^{-1} were related to C=O stretching modes of the anhydride groups while the band near 1690 cm^{-1} was assigned to the C=O stretch of the benzophenone carbonyl. The bands near 1260 and 650 cm^{-1} were assigned to the CO stretching mode and the COC deformation mode of the anhydride groups, respectively. The C=O stretching modes of the anhydride groups are near 1849 and 1763 cm^{-1} in phthalic anhydride while the CO stretching and COC deformation modes are near 1258 and 642 cm^{-1} , respectively (13).

Most of the remaining bands were assigned to modes of the benzene rings using the Wilson numbering system (14, 15). Thus, the bands near 1620 and 1490 cm^{-1} were attributed to the tangential ring stretching modes $\nu(8b)$ and $\nu(19b)$, respectively. The medium intensity bands near 753 and 555 cm^{-1} were assigned to the radial ring stretching modes $\nu(12)$ and $\nu(1)$, respectively. Sharp, medium intensity bands near 1080 and 1140 cm^{-1} were

assigned to the CH in-plane bending modes $\nu(18b)$ and $\nu(15)$, respectively. No effort was made to assign the remaining weak bands in the normal Raman spectrum of BTDA.

The SERS spectrum obtained from a thin film of BTDA deposited on a silver island film from a dilute solution in dimethylformamide (DMF) is shown in Figure 2. The observed bands and assignments are also summarized in Table I. As can be observed from Figures 1 and 2, there were significant differences between the normal Raman and SERS spectra of BTDA. Bands near 1860 and 1785 cm^{-1} which were relatively strong in the normal Raman spectra were very weak in SERS spectra. The band near 1690 cm^{-1} shifted downward in frequency to about 1675 cm^{-1} in SERS spectra. Bands near 1140 and 1115 cm^{-1} in normal Raman spectra were relatively intense in the SERS spectra but overlapped. The band near 1085 cm^{-1} in normal Raman spectra was also prominent in SERS spectra. Bands near 555, 650, and 755 cm^{-1} which were all strong in normal Raman spectra were absent from the SERS spectra.

Several new bands appeared in the SERS spectra of BTDA which were not observed in the normal Raman spectra. Bands were observed near 1580 and 1425 cm^{-1} that were assigned to the asymmetric and symmetric stretching modes $\phi_a(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ of carboxylate groups, indicating that the anhydride groups were adsorbed dissociatively. The assignment of these bands to carboxylate groups is consistent with the disappearance of all of the bands attributed to the anhydride groups, including those near 1860, 1785, 1260, and 650 cm^{-1} . A new band which was not observed in normal Raman spectra appeared near 845 cm^{-1} in SERS

spectra of BTDA. This band may be related to the band near 838 cm^{-1} in the infrared spectra which was assigned to $\nu(11)$, a CH out-of-plane bending mode. However, the band near 845 cm^{-1} in the SERS spectra of BTDA may also be related to $\delta(\text{COO}^-)$, the deformation mode of the carboxylate groups.

Several authors have investigated the selection rules for Raman scattering by molecules adsorbed onto metal substrates. Moskovits developed a theory that was based strictly on electromagnetic effects (16). According to the theory, modes which are normally allowed for the free molecule may appear in surface spectra with considerably different intensities. The strongest lines in the Raman spectra of molecules adsorbed onto metal substrates should correspond to modes that transform the same as α_{zz} where z is the coordinate perpendicular to the metal surface. The next most intense lines should correspond to modes transforming the same as α_{xz} and α_{yz} . The weakest lines should correspond to modes transforming as α_{xy} , α_{xx} , and α_{yy} . Modes transforming as α_{zz} and involving atomic motions mostly perpendicular to the surface were predicted to be especially intense.

Modes which are normally forbidden may appear in the Raman spectra of molecules adsorbed on the surfaces of reflecting substrates for two reasons. One is that the high symmetry molecule may become a lower symmetry surface complex. The other is that quadrupole terms may contribute to the molecular polarizability (17).

If it is assumed that BTDA is planar, the highest possible symmetry is C_{2v}. Since all of the vibrational modes are allowed in the Raman spectra under the C_{2v} point group, there are no normally forbidden modes in the Raman spectra. However, the A₂ modes are inactive in the infrared spectra. Therefore, any bands which appear in the SERS spectra but not the normal Raman spectra must be due to the formation of a new chemical species or to orientation effects.

In that respect, it is interesting to consider the band which was observed near 845 cm⁻¹ in the SERS spectra of BTDA. As indicated above, this band is probably related to $\nu(11)$, a CH out-of-plane bending mode which was observed near 838 cm⁻¹ in the infrared spectra of BTDA, or to $\delta(\text{COO}^-)$. In order for the mode $\delta(\text{COO}^-)$ to appear strongly in SERS spectra, the BTDA molecules would have to be oriented in a manner that would result in large intensity for $\nu_s(\text{COO}^-)$, the symmetric stretching mode of the carboxylate groups. However, reference to Figure 2 indicates that only a very weak band assigned to $\nu_s(\text{COO}^-)$ was observed near 1425 cm⁻¹. Therefore, it was concluded that the band near 845 cm⁻¹ was related to $\nu(11)$ and that BTDA was adsorbed with a flat configuration in which the planes of the molecules were parallel to the surface.

The spectra shown in Figure 3 were obtained from thin films of BTDA which were spin-coated onto silver island films from 0.1% solutions in DMF and then overcoated with thicker films of DGEBA spun from 2%, 4%, and 10% solutions in toluene. No bands characteristic of DGEBA were observed in these spectra which were

essentially identical to SERS spectra of BTDA. These results demonstrate conclusively that SERS is a short range effect restricted to the first few molecular layers adjacent to the silver surface and that the SERS spectra observed here were characteristic of the interface rather than the bulk of the polymer films.

In another series of experiments, SERS spectra were obtained from mixtures of DGEBA and BTDA which were spin-coated onto silver island films from solutions in DMF (see Figure 4). In all cases, the SERS spectra obtained from the mixtures were identical to SERS spectra of BTDA, even when there were five hundred parts of DGEBA to only one part of BTDA in the mixture. These results indicate that BTDA was preferentially adsorbed onto the silver substrate and dissociated to form carboxylate salts.

The results described above are similar to those obtained by Ondrus and Boerio for epoxy/nadic methyl anhydride adhesives (8). As indicated above, they found that NMA was preferentially adsorbed onto aluminum and copper substrates to form carboxylate species. The reaction on aluminum substrates appeared to stop after formation of perhaps a monolayer of carboxylate was formed but the reaction on copper continued, resulting in significant etching of the oxide on the substrate. In the experiments described here, it is not clear whether the reaction terminated after adsorption of a monolayer of carboxylate or continued.

Formation of a carboxylate layer in the interphase is expected to have an adverse effect on the durability of adhesive joints prepared using anhydride curing agents. Reaction of the

curing agent with the substrate will undoubtedly result in a lower degree of cure in the adhesive in the interphase. That will result in greater water uptake during exposure of the joints to moisture or high humidities. Moreover, since the salts formed by reaction of many anhydrides with oxidized metal substrates are at least sparingly soluble in water, it can be expected that osmotic effects will also occur during exposure of the joints to humid environments that will also result in decreased durability.

The experiments described here demonstrate conclusively that SERS can be used for non-destructive characterization of interphases between polymer systems and metal substrates. Considering that the normal Raman scattering by water is quite weak, it should also be possible to investigate the molecular structure of interphases during exposure to aggressive environments such as water.

For some time, it was considered that the cause of failure of aluminum/epoxy bonds during exposure to moisture was related to hydration of the oxide. However, recent evidence suggests that is not the case. The surface-selective nature of SERS and the weak normal Raman scattering of water may enable SERS to be used to determine changes in the molecular structure of the interphase during water uptake.

IV. Conclusions

Surface-enhanced Raman scattering (SERS) is a powerful technique for the non-destructive characterization of interphases between adhesive systems and SERS-active substrates such as copper, silver, and gold. Raman scattering by molecules adjacent

to the substrate is strongly enhanced in SERS but scattering by molecules a few tens of angstroms away from the substrate is not enhanced at all. As a result, SERS is surface-selective and can be used to characterize polymer interphases without interference by normal Raman scattering from the bulk of the polymer.

Normal Raman spectra of benzophenone tetracarboxylic dianhydride (BTDA) were characterized by strong bands near 1785 and 1860 cm^{-1} that were assigned to the anhydride groups, a strong band near 1690 cm^{-1} that was assigned to the benzophenone C=O stretching mode, and by a strong band near 1620 cm^{-1} that was attributed to vibration $\nu(8b)$ of the benzene rings. The bands due to $\nu(8b)$ and to the benzophenone C=O stretching mode were prominent in the SERS spectra of BTDA but the bands related to the anhydride group were missing, indicating that the anhydride groups were hydrolyzed at the silver surface to form carboxylate groups.

A band was observed near 845 cm^{-1} in SERS spectra of BTDA that was related to $\nu(11)$, a CH out-of-plane bending mode. Considering that this band was absent from normal Raman spectra of BTDA, it was concluded that BTDA was adsorbed with a flat configuration in which the planes of the molecules were parallel to the surface.

SERS spectra obtained from a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured against a silver substrate using BTDA as the curing agent were identical to SERS spectra of BTDA and were independent of the epoxy/BTDA ratio. It was concluded that the spectra were characteristic of the interface rather than the bulk

adhesive and that BTDA was preferentially adsorbed onto the silver substrate. SERS spectra obtained from thin films of BTDA adsorbed onto silver and overcoated with thick films of epoxy were identical to spectra of BTDA and showed no evidence of bands related to DGEBA, supporting the conclusion that the SERS spectra obtained from the DGEBA/BTDA adhesive were characteristic of the interfacial region.

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Table I. Proposed band assignments for benzophenone tetracarboxylic dianhydride (BTDA).

Frequency (cm ⁻¹)			Assignment
Raman	SERS	IR	
		3164	
		3103	
1860		1854	ν (C=O), anhydride
1785		1775	ν (C=O), anhydride
1690	1675	1680	ν (C=O), benzophenone
1620	1620	1616	ν (8b)
		1603	ν (8a)
		1580	ν_a (COO ⁻)
1490		1488	ν (19b)
	1425		ν_s (COO ⁻)
1310		1306	ν (7a)
1260	1260	1262	ν (CO)
		1234	
1170	1175	1166	
1140		1134	ν (15)
1115	1115	1111	ν (13)
1085	1085	1093	ν (18b)
970		965	ν (10a)
925	920	927	
910		915	
		903	
890		885	ν (10b)
		866	
	845	838	ν (11)
775		771	
755		740	ν (12)
720		716	
		680	
650			δ (COC)
560		593	ν (1)
		450	

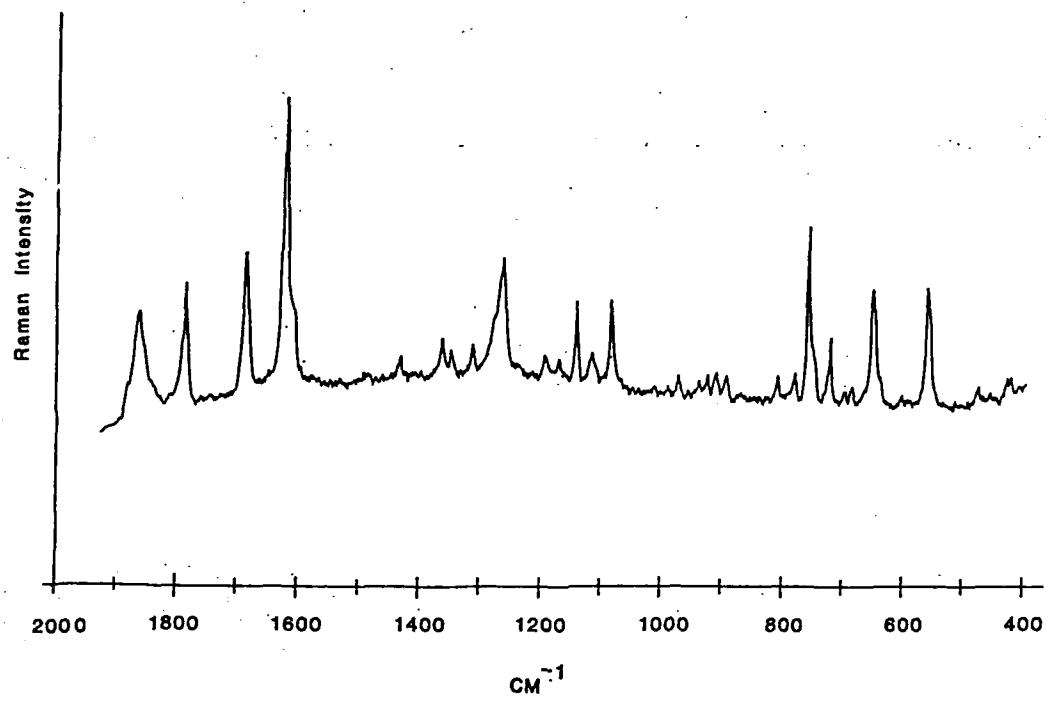


Figure 1. Normal Raman spectrum of benzophenone tetracarboxylic dianhydride (BTDA).

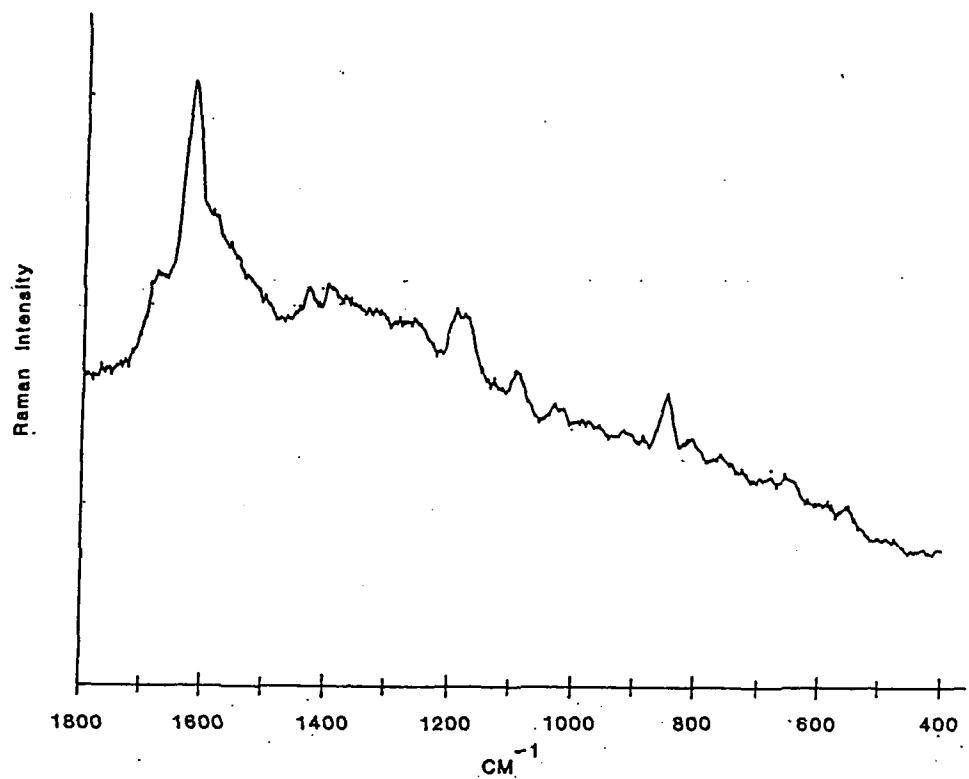


Figure 2. SERS spectrum obtained from BTDA spin-coated onto a silver island film from a 1% solution in dimethylformamide (DMF).

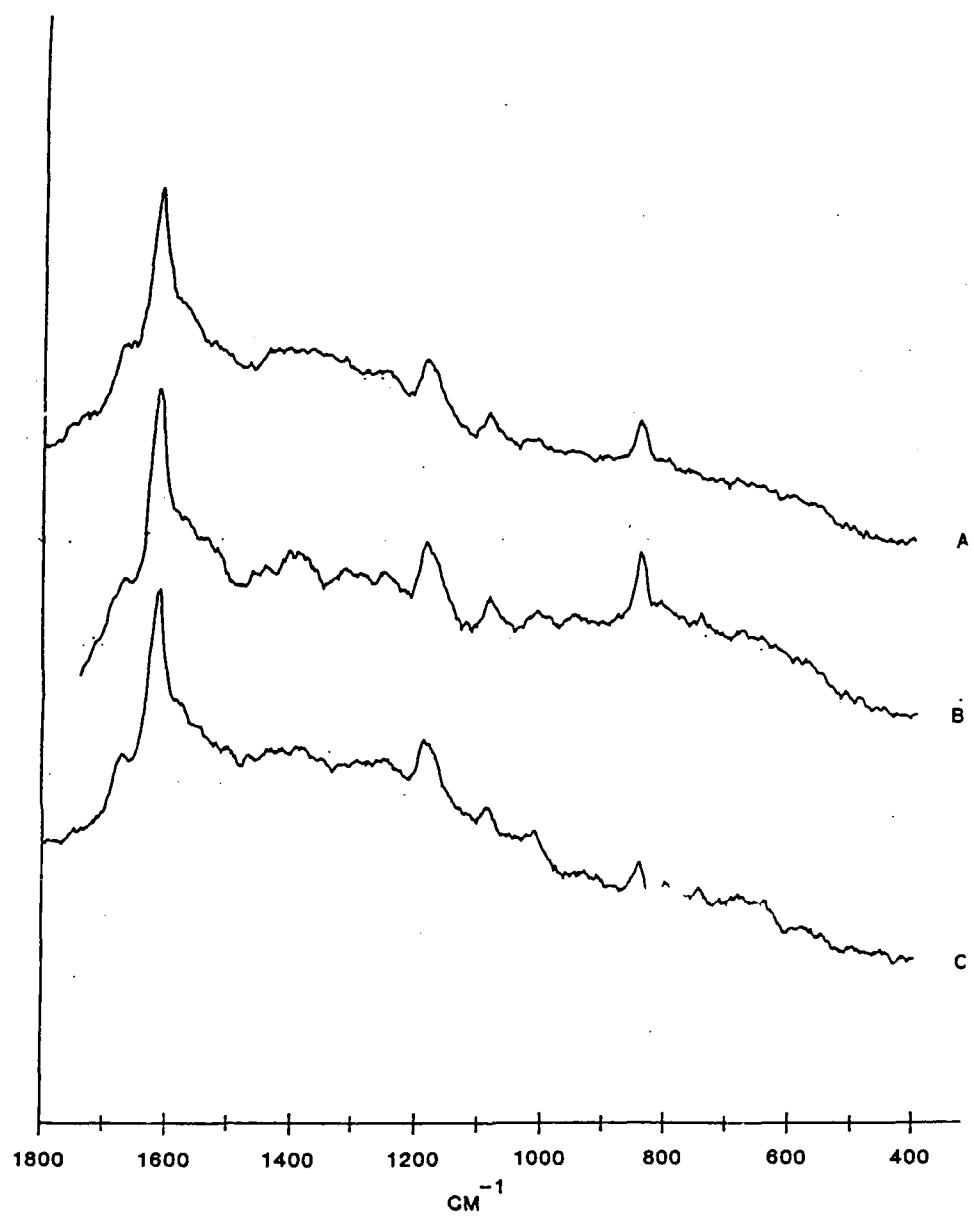


Figure 3. SERS spectra obtained from BTDA spin-coated onto a silver island film from a 1% solution in DMF and then overcoated with DGEBA films spin-coated from (A)-2%, (B)-4%, and (C)-10% solutions in toluene.

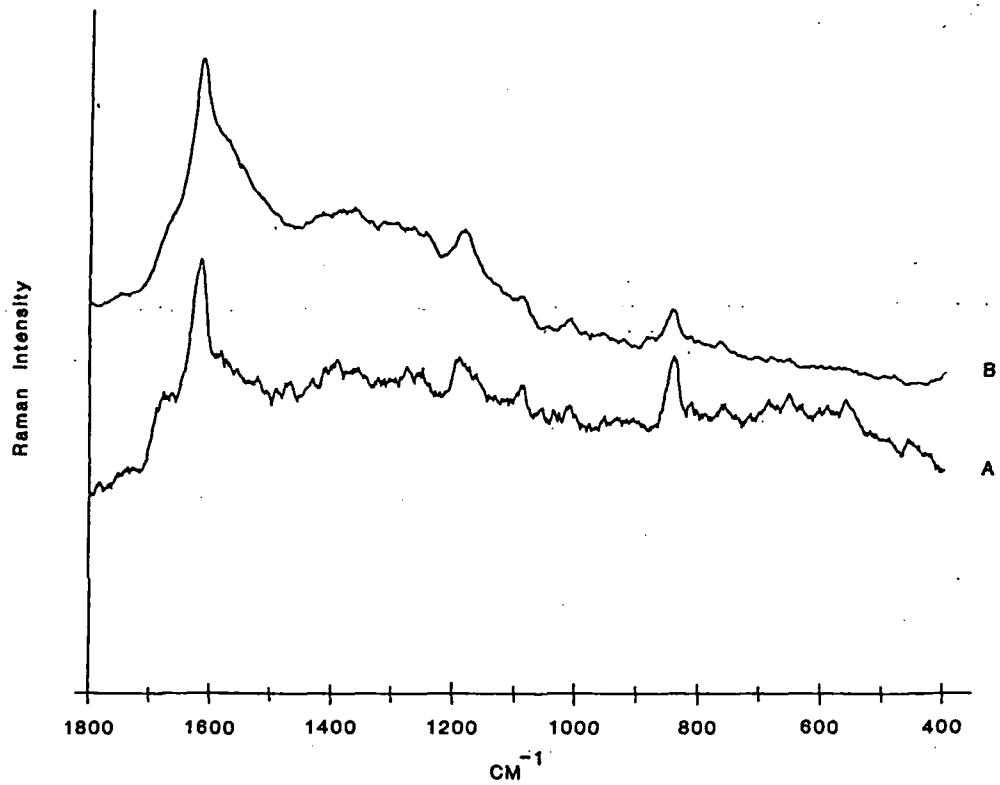


Figure 4. SERS spectra obtained after mixtures of (A) - 0.85 gm of BTDA and 1.0 gm of DGEBA and (B) - 0.01 gm of BTDA and 5.0 gm of DGEBA were spin-coated onto silver island films from 1% solutions in DMF.

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